C
B7476c

Boswell, Maitland C
The course of the oxidation of β-naphthoquinone to phthalic acid.

With the complimen
of the author

THE COURSE OF THE OXIDATION OF β-NAPHTHOQUINONE TO PHTHALIC ACID (to appear in Jour. Phy. Che

AND

THE DETECTION AND ESTIMATION OF α-NAPHTHOQUINONE, β-NAPHTHOQUINONE, PHTHALONIC ACID AND PHTHALIC ACID (to appear in Jour. Amer. Chem. Soc

LIBRARY
OCT 25 1932
UNIVERSITY OF TORONTO

THESIS

PRESENTED TO THE SENATE OF THE UNIVERSITY OF TORONTO
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

MAITLAND C. BOSWELL.

inted at
The University Press,
Toronto.

C
B7476c

THE COURSE OF THE OXIDATION OF β-NAPHTHOQUINONE TO PHTHALIC ACID

AND

THE DETECTION AND ESTIMATION OF α-NAPHTHOQUINONE, β-NAPHTHOQUINONE, PHTHALONIC ACID AND PHTHALIC ACID

THESIS

PRESENTED TO THE SENATE OF THE UNIVERSITY OF TORONTO
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

MAITLAND C. BOSWELL.

Printed at
The University Press,
Toronto.

To the Senate of the University of Toronto:

I beg to recommend that the thesis entitled "The Course of the Oxidation of β-Naphthoquinone to Phthalic Acid, and the Detection and Estimation of α-Naphthoquinone, β-Naphthoquinone, Phthalonic Acid, and Phthalic Acid," submitted by Mr. Maitland C. Boswell, be accepted for the degree of Doctor of Philosophy.

W. LASH MILLER,
Associate-Professor of Physical Chemistry.

Toronto,
December, 1906.

I hereby certify that the thesis above mentioned has been accepted by the Senate of the University of Toronto for the Degree of Doctor of Philosophy in accordance with the terms of the statute in that behalf.

JAMES BREBNER,
Registrar.

The University of Toronto,
December, 1906.

THE COURSE OF THE OXIDATION OF β-NAPHTHOQUINONE TO PHTHALIC ACID.

In many of the reactions of organic chemistry, where the ultimate product is only distantly related to the substances initially present, it is of great interest to trace the intermediate steps of the reaction; either, for example, to elucidate some theory—as that of ring opening in the oxidation of cyclic compounds—or in the hope of discovering constitutional formulas for, and ultimately achieving the synthesis of, the substances experimented on.

Up to the present, information as to the course of such reactions has been sought by examining the reaction products for the intermediate compounds suspected; and by varying the conditions, such as temperature and concentrations of the reaction, or by exchanging one oxidation or reduction agent for another, by adding alkali or acid, etc., to discover, if possible, conditions under which they would be formed in isolable quantities. Much has been accomplished in this manner.

There is, however, a second method of procedure which is illustrated by the experiments of the present paper; and which, so far as I am aware, has not hitherto been put in practice. This consists in studying the behaviour of the suspected intermediate products with the reagents used in the reaction in question, in order to see whether, if formed, they would accumulate in the reaction mixture, or would be converted at once into the final product.

This second method is, in a sense, a complement of the first; each furnishes information that the other cannot give. Failure to isolate any particular substance cannot be regarded as proof that it did not exist temporarily at some stage of the reaction; and on the other hand, proof that the substance in question could not remain unaltered in the presence of the reagents, is proof merely that it might have been—not that it actually was—formed as an intermediate stage of the reaction.

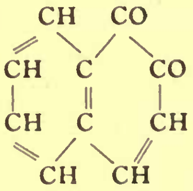
The first method, then, may lead to positive evidence that a given substance is one of the intermediate products of the reaction; the second, to positive evidence that it was not. Neither method can furnish evidence of the kind peculiar to the other.

A few simple experiments carried out by either of the two methods may often give valuable information; but to obtain really conclusive evidence by either of them, all the precautions suggested by the study of chemical kinetics must be observed. In applying the first method, in particular, it has too often been forgotten that change of conditions often entails a radical change in the mechanism of the reaction. An example of such a change is afforded by my experiments on the oxidation of β-naphthoquinone, discussed on page 9.

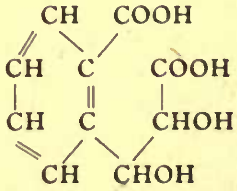
In a paper which will shortly be published, Mr. Daly has made a careful study of some of the likely intermediate stages in the formation of phthalonic acid by the action of potassium permanganate on naphthalene. The present experiments with β-naphthoquinone and some of its possible oxidation products show how, under favorable circumstances, a few simple measurements may lead to equally definite results.

In the oxidation of β-naphthoquinone to phthalic acid,[1] the ring may be broken at the double bond, between the two keto groups, or between the CO and CH groups; of these, the last named seems the least likely, from chemical analogies, while simultaneous dissolution of two or more bonds is least likely of all.

The first alternative would result in the formation of carboxy-phenylglyoxyl-formic acid which on further oxidation might be converted into phthalonic acid and then into phthalic acid (Series A). The experiments of Zincke[2] and of Bamberger and Kitschelt[3] who prepared ortho-carboxy-phenylglyceric acid by the action of chloride of lime on β-naphthoquinone,



β-naphthoquinone



ortho-carboxy-phenylglyceric acid

lend probability to the second supposition (Series B); and I have accordingly undertaken experiments to ascertain whether the oxidation by chromic acid follows the same course.

The first product of the oxidation, if the bond between the two keto groups be broken, would be *o*-carboxy-cinnamic acid. I do not find in the literature any account of this substance having been oxidized without loss of carbon, but cinnamic acid itself gives phenylglyceric acid;[4] *o*-carboxy-phenylglyceric acid may therefore be assumed, with perhaps carboxy-benzoylacetic acid (the hydrate of phthalyl-acetic acid) intermediate. Homophthalic acid, and carboxy-mandelic acid (the hydrate of phthalid-carbonic acid), both of which may be obtained from phthalonic acid by reduction, may also reasonably be regarded as possible stages in the oxidation, since my own experiments show that phthalonic aaid is actually formed.

---

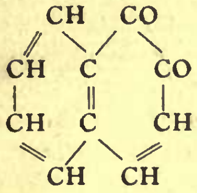
[1] Ann. d. Chem. 189, 155 (1877).

[2] Ber. 25, 400 (1892).

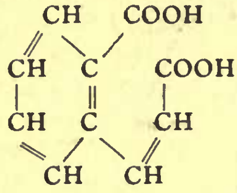
[3] Ber. 25, 888 (1892).

[4] Fittig Ann. d. Chem. 268, 27 (1892).

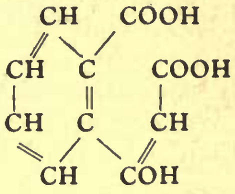
The steps by which β-naphthoquinone is oxidized to phthalic acid, on the assumption that the bond between the two CO groups is the first to break, may thus with some probability be assumed to be:



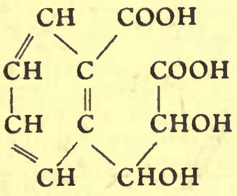
β-Naphthoquinone



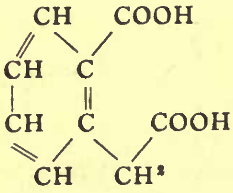
Ortho-carboxy-cinnamic acid



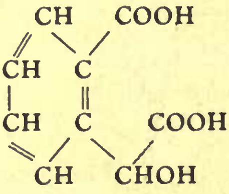
Ortho-carboxy-benzoyl-acetic acid



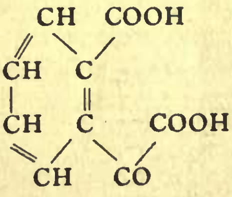
Ortho-carboxy-phenylglyceric acid



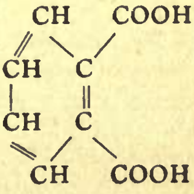
Homophthalic acid



Ortho-carboxy-mandelic acid



Phthalonic acid



Phthalic acid

Substances Used in the Experiments.

β-Naphthoquinone prepared by the method of Lagodzinski and Hardine[1] and purified by the method described in my paper on "analytical methods"[2]; the lactone of ortho-carboxy-phenylglyceric acid, by the method of Zincke[3], melting point 202°; ortho-carboxy cinnamic acid, by the method of Ehrlich and Benedikt[4]; phthalyl-acetic acid, by the method of Gabriel and Neumann[5]; homophthalic acid, by the method of Graebe and Trümpy[6], melting point 174°-175°; the lactone of phthalid-carbonic acid, by the method of Graebe and Trümpy[7], melting point 150°-152°; phthalonic acid, by the method of Graebe and Trümpy[8]. As I found that air dried phthalonic acid does not contain a definite amount of water of crystallization[9], I used anhydrous acid which I prepared by heating the air dried acid at 115° to constant weight. α-Napthoquinone was prepared by the method of Japp and Miller[10] and purified by repeated crystallization from petroleum ether, its melting point was 124°-126°; the α-naphthol and the naphthalene were c.p. preparations of Kahlbaum.

Method of Working.

The rates of oxidation were measured as follows: in a 150 cc. glass stoppered bottle was placed 0.1000 g. β-naphthoquinone (or an amount of one of the other substances proportional to its formula weight); and a mixture of 70 cc. of potassium bichromate solution (7.648 g. $K_2Cr_2O_7$ per litre) with 5 cc. of dilute sulphuric acid (150 g. H_2SO_4 per litre) was added. The bottle was completely immersed in a bath of boiling water; at the expiration of a measured interval it was removed, emptied into a beaker containing 75 cc. ice water and titrated with approximately fortieth-normal ferrous sulphate using potassium ferricyanide as external indicator in the usual way. The results of the measurements are contained in Table I.

---

[1] Ber. **27**, 3075 (1894).

[2] See the following paper.

[3] Ber. **25**, 405 (1892).

[4] Monatsh **9**, 528 (1888).

[5] Ber. **26**, 952 (1893).

[6] Ber. **31**, 375 (1898).

[7] Ber. **31**, 373 (1898).

[8] Ber. **31**, 369 (1898).

[9] See the following paper.

[10] J. Chem. Soc. **39**, 220 (1881).

TABLE I.

SUBSTANCE.	FORMULA.	WEIGHT TAKEN.									P.	T.
β-Naphthoquinone	$C_{10}H_6O_2$	0.1000 g.	t- 2.5 Bi- 4.4	5 14.4	10 21.6	20 27.3	40 31.6	80 37.7	150 41.5	210 45.7	40.5	128
Ortho-carboxy-cinnamic acid	$C_{10}H_8O_4$	0.1215 g.	t- 30 Bi- 9.1	60 12.7	90 18.8	120 19.3	150 21.5	180 21.2			32.4	250
Ortho-carboxy-phenylglyceric acid	$C_{10}H_8O_5$ (Lactone)	0.1317 g.	t- 30 Bi- 1.2	60 5.0	90 9.5	120 12.8	150 17.8	180 21.9			24.3	200
Phthalyl-acetic acid	$C_{10}H_6O_4$	0.1203 g.	t- 30 Bi- 8.5	60 12.7	90 15.1	120 17.2	150 20.6	200 24.6			24.3	200
Homophthalic acid	$C_9H_8O_4$	0.1140 g.	t- 30 Bi- 0.5	90 1.2	120 1.9						16.2	over 1000
Phthalid-carbonic acid	$C_9H_6O_4$ (Lactone)	0.1130 g.	t- 30 Bi- 1.5	60 3.6	90 5.1	120 6.9					8.1	160
Phthalonic acid (anhydrous)	$C_9H_6O_5$	0.1230 g.	t- 40 Bi- 8.2	80 10.2	140 16.9							
Phthalic acid	$C_8H_6O_4$	0.1050 g.	t- 30 Bi- 1.0	60 3.0	90 6.0							

In the first column are the names of the substances; in the second the formulas; in the third the weights taken; in the fourth, after *t* the duration of the oxidation in minutes, and after *Bi* the amount of bichromate reduced expressed in cc. of a solution containing 7.648 g. $K_2Cr_2O_7$ per litre. In the fifth column, under *P*, are entered the number of cc. of bichromate (calculated from the formulas) necessary to oxidize the substance to phthalonic acid, and under *T* the number of minutes (obtained graphically from the data of the table) in which these quantities of bichromate are reduced.

Of course it cannot be assumed that at the moment *T* nothing but phthalonic acid is present in the solution, for that substance itself is oxidized by chromic acid. This reaction, however, takes place slowly in the relatively dilute solution of chromic acid left by the previous oxidation, as is shown in the measurements of Table II.

TABLE II.

PHTH. AC.	BICHR.	SULF. AC.	T	Bi.
0.1230 g.	70 cc.	5 cc.	40 m.	8.2 cc.
.1230	70	5	80	10.2
.0615	70	5	40	2.7
.0615	70	5	80	4.4
.1230	35	5	40	6.0
.1230	35	5	80	8.0
.1230	70	2.5	40	6.3
.1230	70	2.5	80	7.0

The weights of anhydrous phthalonic acid taken are entered under *Phth. Ac.*, the volumes of the bichromate solution and of the acid (page 3) under *Bichr.* and *Sulf. Ac.* respectively, the duration of the oxidation under *T*, and the bichromate reduced under *Bi.* The great effect of the concentrations of the reagents on the rate is sufficiently obvious; from a graph of the results it appears that the rate is proportional to the concentrations of the sulphuric acid and of the bichromate respectively and to the square of that of the phthalonic acid, but for the purposes of this paper it was not necessary to undertake special measurements to establish this relation rigorously.

Far the greater part of the phthalonic acid formed in my experiments would thus escape further oxidation; and, in fact the presence of that substance in each of the solutions at the expiration of *T* minutes was established by the test with potassium permanganate described in my paper on "analytical methods"[1]. This test was carried out as follows. First the chromic acid remaining was reduced with ferrous sulphate. The phthalonic acid was then isolated by neutralizing with sodium carbonate, acidifying with hydrochloric acid, evaporating to dryness on the water bath, extracting with absolute alcohol and evaporating the alcohol extract to dryness; the residue was then dissolved in a little water and filtered. The solution so obtained was acidified with dilute sulphuric acid, and decinormal permanganate was added; in every case the colour was discharged, a reaction characteristic of phthalonic acid and serving to distinguish it from phthalic, homophthalic and phthalid-carbonic acids.

---

[1] See following paper.

Phthalonic acid is thus an isolable product of the oxidation of all six substances studied; similar experiments showed that it is formed by the oxidation of α-naphthoquinone; hitherto it has been known as the product of oxidation of naphthalene[1] and of α-naphthol[2] only.

I.

β-Naphthoquinone.

A glance at Table I shows that the number entered under *T* opposite β-napthoquinone is the smallest in the column. In other words 0.1000 g. of the quinone is oxidized to phthalonic acid in less time than it would take to oxidize any of the hypothetical intermediate oxidation products of series 2 (page 3) even if they had been present in full concentration and had the chromic acid all to themselves.

This shows conclusively that neither orthocarboxy-cinnamic, ortho-carboxy-phenylglyceric, phthalyl-acetic, homophthalic, nor phthalid-carbonic acids can be formed in the course of the oxidation of β-naphthoquinone to phthalic acid; and, as has been pointed out in the introduction, positive evidence of this nature can be obtained in no other way. That phthalonic acid is an intermediate product is shown by the permanganate test described above.

The measurements with *o*-carboxy-phenylglyceric acid are particularly interesting, because the very sample of this substance used in my measurements was itself prepared from β-naphthoquinone by the action of chloride of lime. There was therefore, a priori, a high degree of probability that it would prove one the products of oxidation with chromic acid. Changing the oxidizing agent, however, has changed the whole course of the oxidation. (See page 4).

---

[1] Tscherniac Ber. **31**, 139 (1898); Graebe and Trümpy, Ber. **31**, 369 (1898).

[2] Henriques Ber. **21**, 1607 (1888).

The experimental study of series A was prevented by the circumstance that carboxy - phenylglyoxyl - formic acid has not yet been described in the literature, and that as yet I have had no leisure to attempt its preparation. In the present almost total absence of data of the kinetics of organic reactions, it is impossible to draw any sure conclusions as to its behaviour on oxidation from its formula. The analogous phenylglyoxyl - formic acid, or rather an amino derivative of it, has been prepared by Baeyer and Homolka,[1] but nothing is said as to its behaviour with oxidizing agentt; similarly nothing could be found as to the oxidation of dioxytartaric acid, or diphenyltriketone, both of which likewise contain the group CO. CO. CO. The result of my measurements, then, while conclusively disproving the possibility of the mechanism represented by the formulas of series B, leaves the question open as to series A.

II.

Genetic Relations between the Six Acids.

From the data of Table I, collected in order to study the oxidation of β-naphthoquinone, some information as to the relations of the acids involved may be drawn. It is immediately obvious for instance, that homophthalic acid cannot be an intermediate product of the oxidation of either orthocarboxy - cinnamic, ortho-carboxy - phenylglyceric, or phthalyl-acetic acids to phthalonic acid. Without further study of the relations between rates and concentrations, which (as aside from the main purpose of the research) was not undertaken, nothing further definite can be said; but if the plausible assumption be allowed, that in each case the rate is proportional to at least the first powers of the concentrations of the acids oxidized, then none of the acids studied can be considered as intermediate stages in the oxidation to phthalonic acid of those higher in the table.

III.

α-Naphthoquinone.

In this connection, a few experiments were conducted with α-naphthoquinone the results of which are given in Table III :

TABLE III.

α-Naphthoquinone taken								P	T
0.1000 g.	t	30	60	90	120	150	280		
	Bi	5.1	11.6	20.8	26.2	31.6	35.6	40.5	220

---

[1] Ber. 16, 2219 (1883).

Taken with the data of Table I these measurements show that orthocarboxy-cinnamic and homophthalic acids cannot be intermediate products in the oxidation of α-naphthoquinone to phthalonic acid under the circumstances of my experiments. Without further measurements to ascertain the effect of concentrations on the rates the same cannot be said of ortho-carboxy-phenylglyceric and phthalid-carbonic acids. Consideration of the structural formulas, however, makes it very unlikely. It is possible, however, to show from the data of Tables I and III that phthalyl-acetic acid cannot be an intermediate product.

40.5 cc bichromate are necessary to transform 0.1 g. of α-quinone into phthalonic acid and need 220 minutes to do it. 16.2 cc bichromate would be necessary to oxidize the quinone to phthalyl-acetic acid, and the table shows that this amount of bichromate is reduced in 77 minutes. Experiments on the rate of oxidation of phthalyl-acetic acid show (by interpolation) that in the last (220 – 77) 143 minutes at most 0.51 equivalents[1] of that substance could be oxidized, leaving at least 0.49 equivalents that must have been oxidized in the first 77 minutes. This oxidation would require $0.49 \times 24.3 = 11.9$ cc of bichromate out of the 16.2 actually reduced, leaving only 4.3 reduced by the quinone. The phthalyl-acetic acid formed by the reduction of this amount of bichromate, however, amounts to only $4.3/16.2 = 0.26$ equivalents instead of the minimum of 0.49 required by the assumptions.

The assumption that phthalyl-acetic acid is an intermediate product of the oxidation of α-naphthoquinone to phthalonic acid is therefore disproved by the rate measurements.

The same process of reasoning makes it most improbable that phthalid-carbonic acid can be intermediate in the oxidation of ortho-carboxy-cinnamic acid to phthalonic acid.

IV.

α-*Naphthol.*

The results of a series of experiments with α-naphthol given in table IV show that homophthalic acid cannot be formed "on the way" to phthalonic acid; so far as my experiments go, however, any of the other six compounds studied may be intermediate compounds.

TABLE IV.

α-Naphthol taken							P	T
0.091 g.	t —	30	60	90	150	180		
	Bi. —	18.6	20.1	25.1	26.7	29.2	56.7	580

---

[1] By one "equivalent" is to be understood the weight of substance entered in column 3 of Table I.

V.

The Action of Nitric Acid on Naphthalene.

Laurent[1] and Beilstein[2] have shown that phthalic acid can be prepared by the action of nitric acid, spec. grav. 1.15, on naphthalene, and the latter even stated that "apart from the trouble of working in sealed tubes this is the cheapest way of preparing this substance." I undertook a long series of measurements in the hope of ascertaining the mechanism of this reaction but without success, as in all my experiments—whether carried out in tubes or in open vessels—large quantities of nitro compounds were formed, and conditions could not be found under which oxidation took place anything like quantitatively.

The following table gives the results of a series of determinations of the phthalic acid produced by the action of 40 cc of nitric acid (s.g. 1.15) in six hours at 100° on naphthalene, α and β naphthoquinones, homophthalic, and phthalid-carbonic acids respectively.

TABLE V.

SUBSTANCE.	WEIGHT TAKEN.	PHTHALIC ACID FORMED.
Naphthalene	2.0000	.076
"	2.0000	.074
α-naphthoquinone	0.0712	.057
"	0.0712	.045
β-naphthoquinone	0.0712	.043
"	0.0712	.038
Homophthalic Acid	0.0814	.036
"	0.0814	.047
Phthalic-carbonic Acid	0.0804	.041
"	0.0804	.041

---

[1] Ann. d. Chem. **19** 38 (1836).

[2] Ann. d. Chem. **202** 215 (1880).

THE DETECTION AND ESTIMATION OF α-NAPHTHOQUINONE, β-NAPHTHOQUINONE, PHTHALONIC ACID, AND PHTHALIC ACID.

During the progress of a research upon the mechanism of the oxidation of naphthalene to phthalic acid, it was found necessary to be provided with methods for the detection and accurate determination of α-naphthoquinone, β-naphthoquinone, phthalonic acid, and phthalic acid; and also with a method for the determination of phthalic acid in the mixture of organic acids formed by the oxidation. As no such methods are described in the chemical literature, I was forced to work them out for myself; and after a number of preliminary trials arrived at the following, which have proved very satisfactory, both as to the simplicity of the methods involved, and the accuracy of the results obtained.

Determination of α-Naphthoquinone.

This compound was prepared by the method of Japp and Miller[1] which is an improvement on the method of Groves[2].

The reaction of the quinone which seemed best suited for the purposes of an analytical method is that with stannous chloride, which has been used by Plimpton[3] and by Russig[4] for the preparation of a hydro-naphthoquinone and its derivatives.

In the first experiments I treated the quinone with a large quantity of the stannous salt, and attempted to determine the excess of the latter with decinormal iodine. No satisfactory results, however, were obtained, either at room temperature, or at 100°C. This might be accounted for by the action of iodine on the hydro-naphthoquinone formed by the reduction; but even when the latter was removed results were still unsatisfactory.

The plan was then changed, and the stannous salt was added to the quinone from a burette until the reduction was complete, the end point being recognized by the absence of characteristic colour reactions of the quinone. Two methods of working were studied, differing in the nature of the indicator chosen; both gave good results.

---

[1] J. Chem. Soc. **39**, 220 (1881).

[2] Liebig's Annalen **167**, 357 (1873).

[3] J. Chem. Soc. **37**, 635 (1880).

[4] Jour. Park. Chem. **170**, 32 (1900).

FIRST METHOD: A decinormal solution of stannous chloride in two per cent. hydrochloric acid* is run into the alcoholic solution of the quinone until the yellow colour of the latter is almost discharged. The addition of the stannuous chloride is then proceeded with drop by drop, testing after each addition, on a watch glass, with a drop or two of a mixture of equal volumes of phenyl-hydrazine and alcohol. So long as a trace of the quinone remains a bright pink colour is formed[1].

α-Quinone taken = ~~0.3000~~ 0.0700 g.
Stannous chloride (~~8.52~~ 3.141 g. per l.) required = ~~29.3~~ 32.7 cc.
equivalent to ~~0.307~~ 0.070 g. Quinone

SECOND METHOD: To the alcoholic solution of the quinone, three or four drops of freshly distilled aniline are added, and the whole is boiled; whereupon it turns bright red[2]: Decinormal stannous chloride is then run in from a burette, heating to boiling after each addition, until the red colour is completely discharged. If the end point has been overstepped, a volumetric solution of the naphthoquinone may be used for titrating back.

α-Quinone taken = ~~0.3000~~ 0.0700 g.
Stannous chloride (~~9.37~~ 3.141 g. per l.) required = ~~33.5~~ 33.6 cc.
equivalent to ~~0.308~~ 0.072 g. Quinone

Purification of β-Naphthoquinone.

This compound was prepared according to the method of Lagodzinski and Hardine[3], about 40 g. of crude quinone being obtained from 50 g. β-naphthol. No method could be found in the literature for the purification of this crude material, and attempts to recrystallize it from ether, alcohol, benzene, petroleum ether, acetone and chloroform or mixtures of these were unsuccessful.

The following method based on the reduction of the quinone to the corresponding hydroquinone and subsequent oxidation of the latter, however, effects a complete purification without loss of material.

Twenty grams of the crude dark coloured quinone is placed in a 500 cc Erlenmeyer flask, 250 cc of water saturated with sulphur dioxide is added, the flask is corked tightly and the whole shaken violently for about half a minute or until nearly all is dissolved. The

---

*If the acid is too concentrated, some of Knapp Schultz's amorphous compound may be formed, Am. **210**, 178 (1884).

[1] Ber. **17**, 3026 (1884).

[2] J. Chem. Soc. **37**, 635 (1880).

[3] Ber. **27**, 3075 (1894).

shaking must not be continued too long or there will be a loss due to the separation of hydroquinone from the solution. The mixture is then quickly filtered by suction through a Buchner perforated funnel directly into a solution containing 60 grams potassium bichromate and 40 cc conc. sulphuric acid in 1200 cc water cooled to 5°-10°C. The suction flask should be shaken with a circular motion during the filtration. The pure quinone falls to the bottom as a bright yellow orange precipitate and a black tarry residue remains on the filter. A second portion of twenty grams crude quinone may be dissolved in sulphurous acid as before and filtered into the same oxidizing mixture without removing the quinone already there.

Determination of β-Naphthoquinone.

Decinormal stannous chloride is added from a burette to the quinone dissolved in ether. A dark green, almost opaque solution results, owing, probably, to the formation of a quinhydrone. On adding more tin solution a point is finally reached at which the solution in ether suddenly becomes colourless and transparent, indicating the complete reduction of the quinone to hydroquinone.

β-Quinone taken = ~~0.3000~~ 0.0700 g.
Stannous chloride (~~8.82~~ 5.14 g. per l.) required = ~~21.55~~ 16.5 cc.
equivalent to ~~0.284~~ 0.071 g. Quinone

Purification of Phthalonic Acid.

The syrupy solution prepared from naphthalene and potassium permanganate by the method of Graebe and Trümpy[1] crystallizes on long standing in an exiccator to a solid mass, said to consist of the dihydrate of phthalonic acid[2]; I found it, however, impossible to obtain a preparation of definite composition without completely dehydrating the acid. This is seen from the following determination of the water of crystallization.

1.9676 g. of the pulverized amorphous acid was heated in a steam bath for 5 hours, the loss in weight was 0.2116 g. It was further heated at 115° to constant weight. Total loss in weight 0.2606 g.

	found	*calc.* ($C_9H_6O_5 . 2H_2O$)
H_2O	13.3	15.65

The acid thus contained 2.35% less water of crystallization than corresponds to the dihydrate.

---

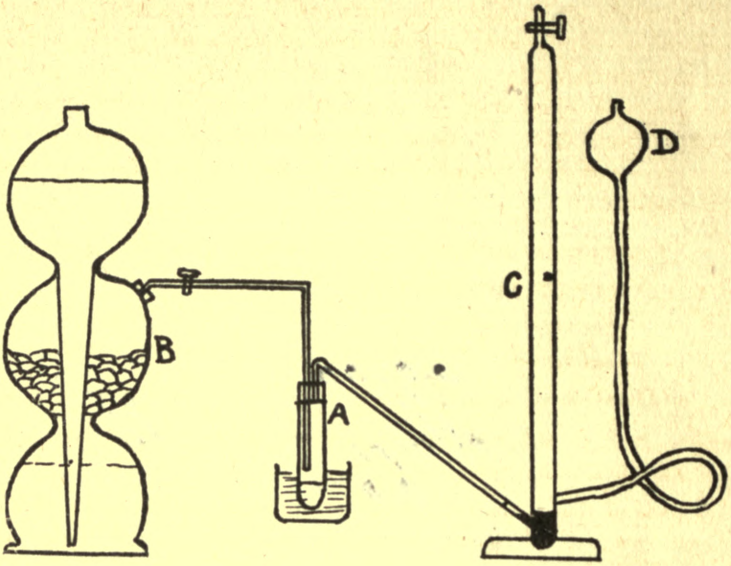
[1] Ber. **31** 369 (1898).

[2] Ibid **370** (1898).

Determination of Phthalonic Acid.

Two methods were devised for the quantitative determination of phthalonic acid, both of which can be quickly and accurately carried out. In the first the carbon monoxide evolved on heating with sulphuric acid is measured, and in the second the phthalonic acid is oxidized by a volumetric solution of potassium permanganate.

FIRST METHOD:



The phthalonic acid, about 0.5 g., is placed in a thick walled hard glass test tube; and 5 cc concentrated sulphuric acid is added. The tube is then fitted with a rubber stopper through which pass two glass tubes, one running to within three quarters of an inch of the surface of the acid and connected with a carbon dioxide apparatus B, the other ending just flush with the bottom of the stopper and connected to the inlet tube of a Schiff's azotometer C containing 30% caustic potash solution. The air is completely expelled by allowing a rapid stream of carbon dioxide to pass through the apparatus, the potash solution during this operation being almost all in the levelling bulb D. When the air is all expelled the tube of the azotometer is filled with the potash solution, and the levelling bulb placed so that the surface of the potash in it is about level with the inlet tube of the azotometer, the mixture of phthalonic acid and sulphuric acid is gradually heated in a paraffine bath to 130° C, when carbon monoxide is quite rapidly evolved. This continues for about ten minutes when the evolution slackens. The temperature is now raised to 140° and in five minutes more the greater part of the carbon monoxide is evolved. At this temperature carbon monoxide would continue to be evolved very slowly for six or seven hours; but if the temperature is raised to 180° the remaining gas is quickly given off, the evolution entirely ceases. The whole duration of the heating is about one hour. The carbon monoxide remaining in the reaction tube is driven over into the azotometer by a stream of carbon dioxide; the levelling bulb is raised so that the pressure inside the azotometer is slightly greater than that of the atmosphere, and the azotometer is disconnected from the heating tube. The carbon monoxide is then transferred to a gas burette filled with a saturated solution of carbon monoxide in water, and after standing half an hour the volume is read, barometer and thermometer being noted. The following results were obtained:

*Anhydrous phthalonic acid, taken - 0.5000 grams
Volume of carbon monoxide - - - 61.1 cc
Barometer reading - - - - - - - 748.5 mm
Temperature - - - - - - - - - 19.0°C.
Tension of aqueous vaper - - - - 17.3 mm

Volume at 0° C and 760 mm pressure = 56.2 cc, equivalent to 0.49 g. of anhydrous phthalonic acid.

A second determination, made immediately after, gave precisely the same volume of carbon monoxide, the pressure and temperature also remaining unchanged.

Another series of experiments showed that when phthalic acid or phthalic anhydride was heated with concentrated sulphuric acid to 210°C, no gas not absorbed by caustic potash solution was evolved.

SECOND METHOD: This method while just as accurate as the preceding has the advantage of being much more rapid; it allows the determination of phthalonic acid in the presence of phthalic, homophthalic and phthalid-carbonic acids.

The phthalonic acid is dissolved in water, sulphuric acid added, and decinormal potassium permanganate run in from a burette. The oxidation is slow at first, but increases in speed as it proceeds, owing probably to the catalytic action of the manganous sulphate formed. The end point can best be obtained by running in an excess of permanganate and titrating back with ferrous sulphate until the last tinge of pink is discharged. By working in this way the end point

---

* Dried at 115° C to constant weight.

can be determined without difficulty within two drops of twentieth-normal ferrous sulphate.

Anhydrous phthalonic acid taken, 0.5000 g.
N/10 Permanganate added, 55.2 cc.
Ferrous sulphate required, = 7.0 cc. equivalent to 3.43 cc permanganate.

Thus 55.2 - 3.43 cc = 51.8 of permanganate were reduced, equivalent to 0.502 g. of anhydrous phthalonic acid.

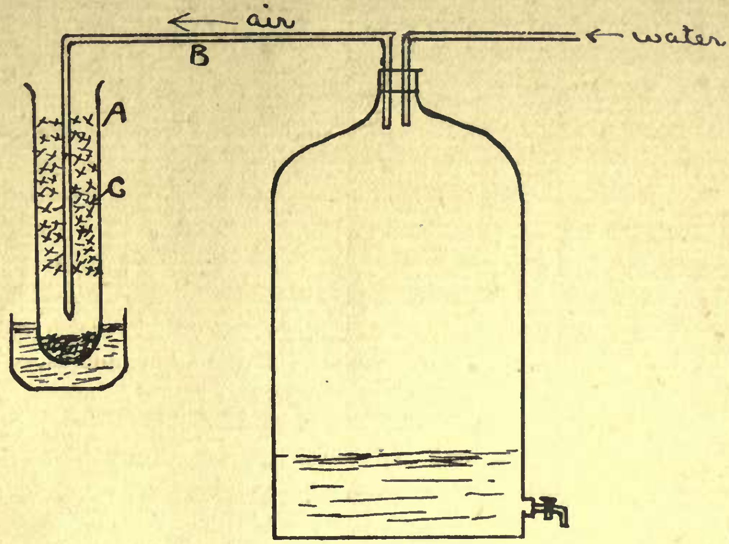
The titration must not be carried out in hot solutions, as in that case homophthalic, phthalid-carbonic, and even phthalic acids are acted on. By adding manganous sulphate to the phthalonic acid before running in the permanganate, the action of the latter is much accelerated.

Separation and Determination of Phthalic Acid.

The method consists in separating the phthalic acid from homophthalic and phthalid-carbonic acids by sublimation, and determining it with volumetric alkali. The apparatus in which the sublimation is effected is made up of the test tube A, the air tube B, and the absorbent cotton C, to catch the sublimed phthalic anhydride. The tube B ends in a fine point about half an inch above the mixture of organic acids in the bottom of the test tube, and is connected with an inverted aspirator.

The test tube is immersed to the depth of ¾ inch in a metal bath kept at 200°-220° C, and a fairly strong current of air directed on to the surface of the acids. After half an hour, the apparatus is removed from the bath ; when cool, the bottom of the test tube is cut off, the cotton is transferred to a beaker and any anhydride adhering to the interior of A or the exterior of B is washed into the the beaker by a volumetric solution of caustic potash. Excess of the potash is then added to the contents of the beaker, and after the cotton has soaked for half an hour in the alkaline solution, the excess of alkali is determined by volumetric sulphuric acid and phenolphthalein taking the usual precautions to avoid errors due to carbon dioxide. A blank experiment shewed that the "Bauer and Black cotton" used was perfectly neutral.

In this connection it should be noted, that phthalic anhydride cannot be determined by caustic potash in the presence of alcohol ; even the alcohol contained in a few drops of phenolphthalein solution used as indicator affects the results, causing the red colour to appear with too little potash. It is necessary therefore, to introduce the indicator in the solid form, or dissolved in the volumetric potash.



The following results show the degree of accuracy of the method :

(1) Phthalic acid - - - -	0.25 g
mixed with homophthalic acid	0.25
and phthalid-carbonic acid -	0.25
Volumetric potash - - -	36.55 cc
Volumetric acid - - -	23.8
equivalent to - - -	26.04 cc potash
Hence potash required =	10.5 cc
This is equivalent to - -	0.252 g. phthalic acid.

(2) Phthalic, homophthalic, and phthalid-carbonic acids, each 0.25 g as in (1).

Volumetric potash - - -	42.8 cc
Volumetric acid - - -	29.75
equivalent to - - -	32.55 cc potash
Hence potash required =	10.25 cc
This is equivalent to - -	0.246 g phthalic acid.

Fluorescein Reaction.

This was carried out in the following manner : One decigram of resorcin was mixed with its own weight or less of the acid to be tested, moistened in a test tube with one drop of concentrated sulphuric acid, and heated to 160° C for three minutes in a bath of sulphuric acid. After cooling, the mass was shaken with 2 cc of a 10% solution of caustic soda, and poured into 500 cc of water.

When resorcin alone is treated as described above, a red solution is obtained with marked blue fluorescence. One decigram of phthalic acid with the resorcin gives a light solution with very strong green fluorescence ; one milligram, a red solution with green fluorescence ; and one fifth milligram, a solution redder than the last, with blue green fluorescence, on comparing it with the solution obtained from resorcin alone the green hue of the fluorescence is distinctly recognizable.

The following substances were also tested, one decigram being used in each case, napthalene, red-pink solution, with green fluorescence ; α-napthoquinone, the same ; β-napthoquinone dark green solution, no fluorescence : α-naphthol, red solution, blue fluorescence ; β-naphthol, the same. In none of these cases was the fluorescence as marked as when one fifth milligram of phthalic acid was employed. Phthalonic acid gave a dark red solution, with strong blue-green fluorescence ; phthalid-carbonic acid, a pink-red solution with green fluorescence, much resembling that obtained from naphthalene ; and homophthalic acid, a slightly red solution, with green fluorescence, almost as strong as when a decigram of phthalic acid was used.

I desire to express my thanks to Professor W. Lash Miller under whose direction this work was performed.

C.
B7476
c

Not aceess

Author Boswell, Maitland Crease

Title The course of the oxidation of p-naphthoquinone to
phthalic acid

University of Toronto
Library

DO NOT
REMOVE
THE
CARD
FROM
THIS
POCKET

Acme Library Card Pocket
LOWE-MARTIN CO. LIMITED